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The Structure of an Aminosilane Coupling Agent in
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ABSTRACT

The molecular structures of partially cured polyaminopropylsilsesquioxane and aminopropyltriethoxysilane in water have been studied using Fourier transform infrared, laser Raman and quasielastic laser light scattering spectroscopy. We propose a multiple hydrogen-bonded structure for the intramolecularly interacting amine and silanol groups using isotope exchange experiment and conformational energy calculations. Conformational restrictions are rather low for the proposed structure thus suitable for the partially cured solid where there are slight perturbations by the surrounding amine and silanol groups. The O....N distance was experimentally determined to be in the range 2.70 - 2.67Å and estimated theoretically as 2.49 - 2.45Å. The aminosilane in very dilute solution was found to be mostly monomeric. The isolated monomer - oligomer transition lies around 0.15% by weight and this transition influences the amount of silane uptake by glass fibers. It is also proposed that this phenomenon may be general for surface treatments by silane coupling agents. Hydrolyzed aminosilane oligomers exist in part as submicron aggregates which can be broken up by the addition of an alcohol. The neutralized aminosilane hydrolyzed very slowly although it dissolved into water instantaneously. A micelle formation was also proposed.

INTRODUCTION

Elucidation of the structures of silane coupling agents in aqueous solution has been given little effort in the past, in spite of its vital importance in determining the physical and mechanical performance of composite materials. This lack of attention is largely due to the limitations in the analytical techniques. Silane coupling agents are effective surface modifying agents of inorganic oxide and metal surfaces. Apparently, surface modification can be achieved by very thin layers of silane coupling agents on the surfaces. For this reason, silanes are usually applied from very dilute aqueous solutions, typically in the concentration range of 0.01 - 1.0% by weight. Only a few techniques are available to study molecular structures of silanes in such dilute aqueous solutions. The weak Raman scattering of water makes laser Raman spectroscopy attractive for this purpose.

Aminofunctional silanes are very useful coupling agents. They form a special family among the many silanes because, unlike other silanes, they dissolve in water instantaneously, the amino silanetriols are extremely unstable in water but they form clear aqueous solutions at wide range of concentration for long periods of time. The stability of silanetriols depend largely on the organofunctionality though they are in general thermally unstable. Phenylsilanetriol and cyclohexylsilanetriol form crystals without major condensation for many months. Eighty-two percent of vinyltrimethoxysilane in fresh 10% by weight aqueous solution exist as vinylsilanetriol (1). Most of neutral silanes including one of the useful silanes, γ -methacryloxypropyltrimethoxysilane (γ -MPS), are believed to contain almost no oligomers in water at concentrations below 1% by weight.

Qualitatively, this is supported by the fact that intensities of the Raman lines of these silanetriols show little dependence on concentration at this concentration level.

However, aminosilanes are generally oligomers even at very dilute solutions. Adsorption of either dimer or higher oligomers are proposed by Schrader (2) after examining adhesive joints which were treated by ^{14}C -labeled γ -aminopropyltriethoxysilane (γ -APS). Plueddemann (1) proposed molecular models of γ -APS along with possibility of low-molecular weight oligomers. Ishida et al. (3) studied aqueous solutions of γ -APS at concentrations between 2 and 80% by weight using Fourier transform infrared spectroscopy (FT-IR). They reported that at this concentration range, γ -APS is oligomeric. To date, no experimental study has been reported elucidating the molecular structure of aminosilanes in aqueous solution at very low concentrations.

Johanson et.al.(4) reported the adsorption of ^{14}C -labeled γ -APS on E-glass fibers from aqueous solution of various concentrations, which showed a breakpoint at around 0.15% by weight. The amount of adsorbed silane increases quickly as the concentration increases up to 0.15% by weight and above this concentration the silane uptake increases more slowly. It is expected from this observation that there may be a transition in the type of molecular structure of γ -APS at this concentration. Transitions of this kind have sometimes been attributed to micelle formation of silanetriols. Vinyltrimethoxysilane (VS) shows the transition for adsorption at 1.5% by weight (5). It was shown that, at this concentration, vinylsilanetriol started forming

micelles. A similar transition was also reported on γ -MPS at 0.4% by weight (6). Again, it was thought to be the onset of micelle formation. Therefore, a similar type of structural origin is expected for γ -APS at 0.15% by weight. It is important to note that micelle formation of the silanetriol immediately leads to oligomer formation for this particular silane because of self-catalyzed condensation. Hence, the previous isolated silanetriol-silanetriol micelle transition will be the isolated silanetriol-silane oligomer transition for γ -APS. However, the best of authors knowledge, none of the papers regarding γ -APS reported the existence of the silanetriol in aqueous solution. Laser Raman spectroscopy provides the opportunity to verify the existence of a silanetriol since silanetriols show a unique and strong Raman line that can be distinguished from the rest of oligomers (7,8).

The size of γ -APS oligomers is of importance when the structure of adsorbed silane layers is under consideration. Absolute particle size can be measured by quasielastic laser light scattering (9). Preliminary attempts using gel permeation chromatography for this application promised little success due to the difficulty of separation. Although larger particles contribute significantly to the quasielastic light scattering data, the determination of absolute particle size and the high sensitivity of this technique enables us to study dilute solutions.

It is apparent from previous studies (1, 3, 10 - 18) that further detailed study is necessary to elucidate the structure of aminofunctional silane coupling agents in partially cured solids as well as in aqueous solutions. Previous reports suggest that the aminosilanes can form intramolecular cyclic structures. As

to the conditions and structures, however, they are still in strong dispute. The intramolecular cyclic structure has been proposed in aqueous solutions (1) and for the partially cured polymer with or without substrates. (3, 12 - 15, 18). The intramolecular zwitterion of the type, $\text{SiO}^- \cdots \text{N}^+\text{H}_3$, has been suggested (12, 14, 18) the hydrogen bonded structures, $\text{SiOH} \cdots \text{NH}_2$ or $\text{SiO}^- \cdots \text{H} \cdots \text{N}^+\text{H}_2$, also have been considered (3, 14, 15).

We have suggested (3) that the intramolecular zwitterion, $\text{SiO}^- \cdots \text{N}^+\text{H}_3$, is unlikely either in an aqueous solution or in partially cured polymer based on the band assignments of the SiO^- and SiOH vibrational modes. No evidence was obtained to verify the existence of a pentacoordinated silicon atom where the nitrogen atom donates the electrons to the silicon atom (1). It was thought that the susceptibility of the NH_2 and SiOH groups to moisture and deuteration might provide insights to the conformations of the aminopropyl chain.

EXPERIMENTAL

A Fourier transform infrared spectrophotometer (Digilab FTS-14) was used at a resolution of 2 cm^{-1} with 300 scans for the purpose of signal averaging. The spectrometer was constantly purged with dry nitrogen gas.

For obtaining laser Raman spectra, an Ar^+ ion laser with 488.0 nm line and 500 mW output-power was used as an excitation source. A holographic grating double monochromator (Spex 1402) was equipped with photomultiplier tube (RCA 31032) and usual photon counting electronics. Spectral resolution was 5 cm^{-1} at the excitation frequency unless otherwise mentioned. Scanning speed was in the range $0.1 - 0.5 \text{ cm}^{-1}/\text{s}$ and the time constant was adjusted accordingly.

Quasi-elastic laser light scattering experiments were performed with Ar^+ ion laser with 488.0 nm and 100 mW output-power. The system was equipped with the devices for photon counting and obtaining autocorrelation function. A detailed description of the setup has been reported elsewhere (19).

Gamma-aminopropyltriethoxysilane (γ -APS) was purchased from Petrarch Systems Inc. A freshly purchased sample was stored under nitrogen atmosphere and was used for the infrared and Raman experiments and a vacuum distilled sample was used for the light scattering experiments. D_2O had an atomic purity of 99.8% and used as received while only deionized, distilled H_2O was used.

The aqueous solution of γ -APS was prepared initially as a 20% by weight and dried on a AgBr plate at room temperature with relative humidity $50 \pm 10\%$ except for the deuterated samples which were dried in the nitrogen atmosphere. For the infrared experiments, the position of the substrate was fixed to a sample holder so that the same amount of the sample could be maintained before and after the treatments, thus one could perform 1:1 subtraction without the benefit of an internal thickness band when difference spectroscopy is desired. A polyaminopropylsilsesquioxane film on a substrate was exposed either to H_2O or D_2O for 15 min in a closed beaker unless otherwise mentioned.

The effect of moisture was studied by controlling the humidity using P_2O_5 for the dry air and KOH aqueous solution for the CO_2 free wet air. The polyaminopropylsilsesquioxane film on a substrate which was dried in the nitrogen atmosphere for a few hours was kept in the closed glass vial with controlled atmosphere for 130 hrs at room temperature. In order to examine the possible effect of the AgBr substrate to the structural changes of the

aminosilane, an AgBr plate which was dip coated with a thin polyethylene film was used in one case where the effect of saturated water vapor was in question.

RESULTS

The spectrum of polyaminopropylsilsesquioxane prepared from 20% by weight H_2O solution is shown in figure 1-A in which characteristic intensification of amine and its related bands is seen. When the polyaminopropylsilsesquioxane film on an AgBr substrate is dried in air at room temperature for 1 hr and then exposed to D_2O vapor for 2 hrs, the spectral features changed somewhat but still showed the characteristic intensified bands. The same result was obtained for 24 hrs deuteration indicating a strong resistance to deuteration. The expected OD or ND stretching bands are seen in the range $2700 - 2000\text{ cm}^{-1}$ while OH or NH stretching modes in the region $3500 - 2500\text{ cm}^{-1}$ still appear. A noticeable amount of free amine groups, that are characterized by the multiple bands at $3435, 3350$ and 3284 cm^{-1} , are present in the polyaminopropylsilsesquioxane, which become a featureless broad band centered at 3300 cm^{-1} upon deuteration. A weak band at 2498 cm^{-1} , with very weak multiple bands nearby, are due to ND groups and ND_2 groups.

Two strong bands at 1570 and 1484 cm^{-1} shifted to 1540 and 1463 cm^{-1} , respectively, upon deuteration. A new strong band at 1423 cm^{-1} in the spectrum B is assigned to the NHD bending mode. Another strong band at 1328 cm^{-1} disappeared while a band at 1200 cm^{-1} , an overlapping band at 1193 cm^{-1} and a new band at 1210 cm^{-1} , slightly intensified. The new band at 1210 cm^{-1} can be assigned to the ND_2 bending vibration. The band at 966 cm^{-1} , in the region of

SiO^- and SiOH vibrations, which we have previously eliminated the possibility of SiO^- stretching mode (3), diminished after the deuteration indicating the correctness of our previous assignment since the SiO^- band is obviously unaffected by the deuteration. The SiO stretching mode of the residual SiOH groups gives rise to a band at 951 cm^{-1} which negligibly shifted to 932 cm^{-1} upon deuteration.

When γ -APS is initially hydrolyzed by D_2O and dried in a nitrogen atmosphere, the spectral features (figure 2-A) are remarkably different from the polyaminopropylsilsesquioxane deuterated after the polymer is formed and partially cured (figure 1-B). No indication of intensification is seen in the amine bands. The multiple bands at 2495 , 2415 and 2350 cm^{-1} indicate nearly complete conversion of NH_2 into ND_2 with a small amount of NHD impurity seen at 3280 cm^{-1} . No broad band is seen around 2950 cm^{-1} . The weak band at 1552 cm^{-1} is probably the bending mode of the NHD impurity which is seen at 1542 cm^{-1} in figure 1-B. A prominent band at 1207 cm^{-1} is the ND_2 bending mode as the major contribution. The SiO stretching mode which was observed at 931 cm^{-1} for the SiOH groups in figure 1-A appeared at 935 cm^{-1} (figure 2-A) indicating the conversion into the SiOD groups (7, 8).

After a brief exposure of the deuterated polyaminopropylsilsesquioxane to H_2O , interesting changes occurred. Most noticeable of all are the amine bands which show no intensification. The multiple bands at 3340 , 3270 and 3155 cm^{-1} appeared after protonation leaving a very weak singlet at 2420 cm^{-1} due to the ND stretching mode of the NHD group. The weak bands at 1552 cm^{-1} shifted to 1590 cm^{-1} which can be assigned to the NH_2 bending mode of the weakly hydrogen bonded amine. This type of amine group will be synonymously described as a free amine in this

paper. The band at 1207 cm^{-1} weakened considerably revealing the band at 1193 cm^{-1} resulting in the average peak position at 1195 cm^{-1} , indicating that the most of the ND_2 groups available for protonation are converted back to the NH_2 groups. Worth noticing is the band at 936 cm^{-1} whose frequency indicates the dominating presence of the SiOD groups even after the exposure to H_2O vapor.

Figure 3 shows the effect of dry air to the structure of partially cured polyaminopropylsilsequioxane. Only slight spectral changes have been observed in dry air. The difference spectrum (spectrum C) shows that a broad band centered at 3200 cm^{-1} decreases as well as the band at 912 cm^{-1} . Those bands are assigned to the OH and SiO stretching modes of the residual SiOH, respectively.

Humid air, on the other hand, has a dramatic effect on the spectrum of the polyaminopropylsilsequioxane shown in figure 4. Almost all characteristic intensified bands related to the amine group decreased in intensity and the resultant spectrum is similar to the unhydrolyzed γ -APS with respect to the amine bands (3, 15).

In order to verify the effect of water on the aminosilane, a polyethylene coated AgBr plate was used and the same humidity treatment was given. Unlike previous spectra in figure 4, almost identical spectra, as in figure 3, for the dry air treatment are obtained in this case and the spectra are shown in figure 5. Although the spectra shown here are obtained after 1 week humidity treatment and additional 1 week treatment at room temperature with relative humidity of $40 \pm 10\%$, the spectra obtained after 1 week humidity treatment were very similar to the ones shown in figure 5 except the peaks due to the water adsorbed in the polyethylene coating.

Since the structure of silanes in the treating solution is reported to influence strongly the structure of the silane layers on glass fiber surfaces, our attention was further focused on the aminosilane hydrolyzate in different concentrations in water. Laser Raman spectroscopy can detect organosilanetriol uniquely and, in general, a strong line is observed in the range $725 - 625 \text{ cm}^{-1}$ due to the symmetric stretching mode of the silanetriol. A very weak line at 712 cm^{-1} is observed in the 10% by weight aqueous solution which lies within the typical SiO symmetric stretching mode of silanetriols with more than three carbons on their organofunctionality (figure 6). When the concentration was reduced to 0.5% by weight, the relative intensity of the 712 cm^{-1} line significantly increased compared to the 881 cm^{-1} line which is due to the ethanol produced as a byproduct of the hydrolysis. Assuming the complete hydrolysis which is supported by the infrared evidence (3), one can use the 881 cm^{-1} line as an internal standard. Since no other line is expected around 712 cm^{-1} other than the silanetriol, we assign this line to the symmetric stretching mode of the aminopropylsilanetriol and consider this observation to be the evidence of the existence of hydrolyzed monomer in water.

The relative intensity designated as I_{712}/I_{881} is proportional to monomer content and plotted in figure 7 against the concentration of the silane. The monomer content increased gradually when the concentration is reduced to about 1% by weight. Then a sudden increase in the monomer content is seen below 1% by weight until 0.25% by weight which is the lowest concentration examined. Below 0.1% by weight, the analysis becomes extremely difficult due to the strong Rayleigh scattering of water and the high noise level. The fact that the intensity of the 712 cm^{-1} increases as the concentration decreased also provides indirect support for the assignment of this line because the monomer concentration always increases when the concentration decreases.

The relative intensity ratio I_{712}/I_{881} is read from the curve in figure 7 in the concentration range 0 - 1.0% by weight (figure 8). In the same figure, the amount of adsorbed ^{14}C -labeled γ -APS reported by Johansson et al. (4) is replotted as a function of the concentration. One can observe a breakpoint in the amount of adsorbed silane at around 0.15% by weight which corresponds to the concentration where a large amount of silanetriols exist in the solution.

In general, a fresh silane solution in the concentration near several percent by weight contains mostly silanetriols. However, as we have seen so far, the aminosilane produces mostly oligomers even at 1% by weight. The pronounced instability of aminopropylsilanetriol is considered to be due to the self-catalyzed condensation of the silanetriols by the amine group. This can be confirmed by neutralizing the amine group by acetic acid prior to the hydrolysis. Figure 9 shows an example of the Raman spectrum where γ -APS is first neutralized with acetic acid and then hydrolyzed so that the concentration of the aminosilane became 5% by weight in the aqueous solution. Also shown in the same figure is the Raman spectrum of pure acetic acid although the peak positions do not agree exactly due to the salt formation with the amine groups. Nonetheless, one can distinguish easily the modes due to the aminosilane, with the help of the Raman spectrum of 5% by weight γ -APS in water without acetic acid (Spectrum A).

Figure 10 shows the relative intensities I_{712}/I_{1048} as a function of the mole ratio of acetic acid to aminosilane. Since the baseline of the alcohol C-O stretching mode at 881 cm^{-1} is influenced by the COO^- line of the acetic acid around 930 cm^{-1} , the line at 1048 cm^{-1} due to the antisymmetric COO^- stretching mode of the ethanol is used as an internal standard. When the

aminosilane and acetic acid becomes equimolar, the mixture yields a much larger concentration of silanetriols. More addition of acetic acid increases the concentration of the silanetriols. After passing the the neutral point, the acetic acid salt of the aminosilane is expected to behave similar to neutral silanes. At the concentration employed, most of the silane is believed to be silanetriols. Since the conversion factor I_{881}/I_{1048} is measured to be 3.0, the results in figure 7 and 10 can be compared. The highest silanetriol concentration in figure 10 has the relative intensity $I_{712}/I_{1048}=0.77$ which is converted to be $I_{712}/I_{881}=0.26$. The observed relative intensity for the 0.25% by weight solution is $I_{712}/I_{881}=0.32$. If the silanetriol concentration is 100%, this ratio should be 0.26. However, the small discrepancy can be explained because we assumed that the 5% by weight solution contains 100% silanetriol, which is not correct. Nonetheless, we can qualitatively conclude that the most of the aminosilane below 0.25% by weight is monomeric.

It was noticed that when the aminosilane/acetic acid mixture is not stoichiometric, the aqueous solution quickly reaches the steady state. However, the stoichiometric mixture changed its spectral characteristics slowly over days. The hydrolysis kinetics was followed for this mixture (figure 11). A few notable facts are that the silane undergoes very slow hydrolysis at room temperature and reaches the final stage after 2000 min. The concentration of the silanetriol reaches a maximum at around 500 min and reduces somewhat finally reaching an almost constant concentration. The silane does not complete hydrolysis and small amount of unhydrolyzed monomers remain. This observation is consistent with the report which states that unhydrolyzed cationic vinylbenzyl type coupling agent was recovered as unhydrolyzed monomer after mixing with water (20). Since this silane is partially neutralized with

hydrochloric acid, the salt on the long tail may be protruded around the micelle of the silane (21) preventing hydrolysis of the alkoxy groups which is within the micelle. Similar effects are probably taking place with the γ -APS/acetic acid mixture. The particle size of the micelle is rather large in the order of the wavelength of the visible light since the Tyndal phenomenon is observed for the solution.

The salt formation is not the requirement to observe a large silane particle in water. The hydrodynamic radii of hydrolyzed γ -APS at various concentrations measured by quasi-elastic laser light scattering spectroscopy is shown in figure 11. When the γ -APS (as received) was used, a straight line is obtained and the particle size even at a concentration of 0.1% by weight could be measured. However, when the γ -APS is vacuum distilled immediately prior to the use, a different curve resulted and the observation below 1% by weight was virtually impossible due to the very weak scattering. This difference probably arises because the (as received) sample gradually hydrolyzes with the small amount of moisture still available and condenses to form microgel particles.

When the 10 % by weight aqueous sample with distilled material was diluted with ethanol to make 5 % by weight silane solution, the particle size became too small to observe, clearly indicating that the hydrodynamic radii observed are not due to one unseparable molecule but due to the aggregates of smaller molecules. This is consistent with the observations that the Raman spectrum shows the presence of a small amount of monomers.

It should be mentioned, however, that the hydrodynamic radii obtained by the light scattering measurements represent the larger particle side of the

distribution since the scattering intensity is proportional to the 6th power of the diameter. Hence, the observed values should be interpreted as the upper limit of the particle size rather than the average.

CONFORMATIONAL ENERGY CALCULATIONS

Multidimensional minimization techniques have been used to predict the stable intramolecular conformations of molecules, including polymer chains (22, 23). These calculations involve the minimization of the free energy of the system as a function of the structural variables. The internal energy contribution to the free energy is calculated via interatomic potential functions.

In the molecular mechanics framework, the interatomic pair potentials are considered pairwise additive and normally constitute two main contributions: a parametrized dispersive/repulsive term to define steric interactions, and secondly a Coulomb term to include the electrostatic monopole-monopole interactions. The possibility of hydrogen bonding is treated through a separately parametrized hydrogen bonding function in our molecular mechanics framework. For internal rotation about specific bonds a suitable torsional energy function is also included. (24).

In most conformational calculations the valence geometry is fixed so that the bonded atom interaction energy contribution to the total energy is constant. Thus, in our calculations the internal rotation angles were considered to be the only structural variables. The conformational calculations for the silane molecule was carried out using our molecular mechanics software system CHEMLAB (formerly Camseq-II) (24). The built-in potential energy function between an atom pair i,j is represented in the following form:

$$\phi_{ij} = \frac{-A_{ij}}{r_{ij}^6} + \frac{B_{ij}}{r_{ij}^{12}} + \frac{q_i q_j}{\epsilon r_{ij}}$$

where r_{ij} is the interatomic distance and q_i, q_j are the partial charges in eu's. The silicon A and B parameters are not available in the literature and thus were calculated using the modified Slater-Kirkwood relationship: (25)

$$A_{ij} = \frac{\frac{3}{2} e\hbar/m^{1/2} \alpha_i \alpha_j}{\left(\frac{\alpha_i}{N_{i \text{ eff}}}\right)^{1/2} + \left(\frac{\alpha_j}{N_{j \text{ eff}}}\right)^{1/2}}$$

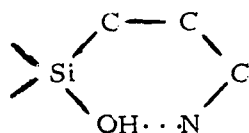
where the atomic polarizability α for Silicon is taken from Benderson et al. (26). These values are reported within an accuracy of $\pm 2\%$. The partial charges were calculated using the CNDO/2 techniques. The fixed dielectric of 3.6 was used in all the calculations.

The energy minima can be located using one of two different approaches. One method is to scan the parameter space with a fine grid and subsequently pick out the relative minima. The second approach is to use an optimization technique to find an effort path leading to a minimum. In the present problem the first approach for the 7 backbone bond rotations at 30° intervals will involve 12^7 conformations. The second approach, on the other hand, may miss some relative minima. In our problem we make a judicious combination of these two approaches. First, a random scan about the 7 backbone bonds was performed and the relative minima were picked up. Subsequently these structures were optimized using a nonlinear optimization technique based on Davidon-Fletcher-Powell algorithm.

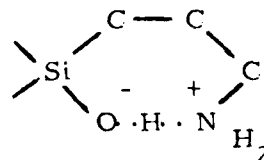
Among 10,000 conformations randomly examined, we have observed 30 energy minima which were then minimized in conformational energy as described above. These 30 energy minima had total conformational energies of less than -24 kcal/mole. The energy calculations based on the physical significance, we obtained 3 unique structures which are shown in figure 12, 13, and 14, whose total conformational energies are -26.3, -26.6 and -27.7 kcal/mole, respectively. It should be mentioned that these conformations were calculated for the γ -aminopropylsilanetriol in free space and no intermolecular interactions were taken into account.

DISCUSSION

The susceptibility to deuteration of polyaminopropylsilsesquioxane, the resistance of the amine groups as well as the silanol groups in the incompletely cured solids, suggests that the structure (I) and (II) need to be modified.

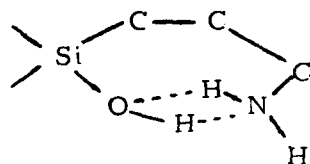


(I)



(II)

No papers concerning the structure of aminofunctional silanes considered steric factors nor multiple hydrogen bonding. The fact that the SiOH and one of the amine protons are not easily deuterated leads us to propose the following multiply hydrogen-bonded structure (III).



(III)

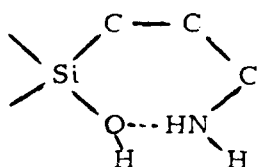
All-cis structure in the propyl chain brings the nitrogen atom too close to the oxygens, which would create very strong steric repulsive forces. One of the most stable conformations would be the structure similar to cyclohexane. Therefore, the silicon, nitrogen, C¹ and C³ atoms form a plane and the C² atom lies out of the plane. This structure would yield the O...N distance in the range 2.5 - 3.0 Å, a typical hydrogen bonding distance. In this structure, one of the amine protons is restricted in motion by hydrogen bonding while another proton is free.

The hydrogen bonded structure (III) intensifies the bands related to the amine group and predominates the infrared spectrum. The amine groups of the spectrum A in figure 2 appear to be mostly ND₂ since there is only a weak band at 3280 cm⁻¹ of the NHD. It is also reflected in the strong 1207 cm⁻¹ band of the ND₂ bending mode overlapping with the band at 1193 cm⁻¹. After a brief period of protonation, the intensity decreased significantly and the resultant peak at 1195 cm⁻¹ is mostly due to the band at 1193 cm⁻¹. Thus, most of the ND₂ groups are susceptible to the protonation implying the presence of a large amount of free amine groups. This is also supported by the observation of multiple bands in the range 3350 - 3100 cm⁻¹. Although a straightforward comparison cannot be made due to the complication of the bands, the intensity of the multiple bands mass adjusted by the CH stretching mode at 2932 cm⁻¹ is approximately 50% of the partially cured sample.

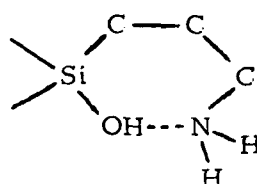
In spite of the predominant conversion of the deuterated amine to protonated amine, the characteristic intensification of the amine bands does not appear. It is possible that the amine groups represented by the weak band at 2420 cm⁻¹

mainly due to the ND stretching mode of the NHD group may be partly responsible for the non-intensification of the amine bands. A dramatic intensity decrease upon deuterium exchange is also seen for the NH group existing as a chemical defect in $(\text{SN})_x$ polymer (27). Worth mentioning is that most of the silanol groups still remain as SiOD groups. Therefore, it is difficult to distinguish the origin of the intensification.

The structure (III) provides the structural basis for the resistance to isotope exchange in both silanol and one of the amine proton. It is also possible that the hydrogen-bonded structure is a mixture of structures (IV) and (V).



(IV)



(V)

However, the mixture theory is unlikely the predominating one. If structure (VI) occupies an appreciable amount of hydrogen bonded species, it cannot explain the resistance of silanol groups to isotope exchange. As previously stated, the silanol band shows almost no change in frequency upon isotope exchange. This leads to the structure (V) to be the predominating species, where the amine group should be easily isotopically exchanged. The results in figure 1 apparently disregard this possibility. While there is still reservation as to the proposed model because the effect of siloxane network to

the penetration of water molecules is not well understood, the structure (III) is more favorable based on our experimental facts.

According to Lord et al., Nakamoto et al. and other researchers (28 - 30), the $A \cdots B$ distance in hydrogen bonded solids can be measured by the AH stretching frequency. The $A \cdots B$ distance / AH stretching frequency correlation is a function of the type of hydrogen bonding. In other words, the $OH \cdots N$ bond has a different functionality to describe the $O \cdots N$ distance than the $O \cdots HN$ bond. If the structure (III) is the case, the $O \cdots N$ distance calculated from both relations should coincide. Assuming that the relationships described by Nakamoto et al. are also valid in an intramolecularly hydrogen-bonded amorphous solid, the $O \cdots N$ distance from the NH stretching frequency at $2900-2850 \text{ cm}^{-1}$ is $2.70 - 2.67 \text{ \AA}$ while the $O \cdots N$ distance from the OH stretching frequency at $3150-3100 \text{ cm}^{-1}$ is $2.77 - 2.67 \text{ \AA}$. The good agreement, within the experimental error, in $O \cdots N$ distance by both $OH \cdots N$ and $O \cdots HN$ relationships provide further favorable support for structure (III).

Since we used the silanetriol in free space for the energy calculations, there are some unlikely conformations in the 30 minima when a partially cured silane film is considered. For example, the existence of silanetriols and diols are unlikely. Degeneracy, conformations involving more than two silanols, and the conformations which did not involve hydrogen bonding were eliminated. As a result, we obtained three unique conformations which had physical significance. The structure in figure 12 is the multiply hydrogen bonded structure proposed experimentally. It is worth mentioning that the experimental and theoretical conclusions were obtained quite independently. The calculated $O \cdots N$ distance

is 2.45 Å while experimental value is 2.70 - 2.67 Å. This difference is reasonable because in our calculations possible intermolecular interactions were not considered. Intermolecular interactions such as hydrogen bonding likely reduces the intramolecular interactions and tend to free the amine group resulting in slightly widened O...N distance.

Another multiple hydrogen bonding in figure 14 is convenient to explain the observations that some NH_2 groups are resistant to deuterium exchange (figure 1 spectrum B). The structures in figures 14 and 15 have lower energy minima than the one in figure 13. However, these conformations are fairly constrained. While the conformation in figure 13 appears rather insensitive to bond rotation. Therefore, when there are slight perturbations due to intermolecular interactions, the probability of having the structure in figure 13 increases.

It should be mentioned that the silanol condensation without involving the amine group also shows an intensity decrease around 3200 cm^{-1} as evident in figures 3 and 5. Therefore, there are some silanols which are not strongly interacting with the amine groups. It is possible that these silanols show a broad band which is overlapping with the band due to the silanol in the intramolecular cyclic structure. The intensity decrease of the broad band in the range $3600 - 2000\text{ cm}^{-1}$ in figure 4 shows a somewhat asymmetric band shape, which seems to have another broad band around $3150 - 3100\text{ cm}^{-1}$, possibly due to the above mentioned cyclic structure. The broadness of the peak and overlapping bands due to the NH stretching modes of free amine make analysis difficult.

The band shape of the NH stretching mode of the strongly interacting amine groups is similar to amine salts such as $\text{RNH}_3^+\text{Cl}^-$ and $\text{RR}'\text{NH}_2^+\text{Cl}^-$. A very broad band with fine structure and a characteristic weak band in the region

2400 - 1800 cm^{-1} are observed for amine salts. It is likely that some of the amine groups interact with CO_2 in air and form a linear-chain amine salt since organic primary amines are susceptible to CO_2 contamination. Based on the observation of NH_2 groups, it is apparent that the partially cured polyamino-propylsilsesquioxane is a mixture of various amines.

It is interesting to notice that only the uncoated AgBr plate in a humid air shows a dramatic effect on the structure of the amine group. It is possible that the high humidity increases the water content in the silane film on the AgBr plate and slightly dissolves AgBr. The AgBr then dissociates to the Ag^+ that can chelate to the nitrogen atom. This action reduces the strength of the hydrogen bonding between the amine and silanol and increases the freedom of the silanol groups, resulting in the condensation of the silanol groups. When the sample was dried in order to take the infrared spectrum, the Ag^+ reforms AgBr salt with the Br^- ion and frees the amine groups. The polyethylene coating obviously inhibits the migration of the Ag^+ to the silane film in a week.

The correlation between the silanetriol content and the amount of adsorbed silane on the surface of glass fibers shown in figure 7 leads to an interesting general trend in surface modification with silane coupling agents. The breakpoint around 0.15% by weight in the silane uptake almost coincides with the concentration of the silane solution at which most of the aminosilane becomes monomeric. A similar trend has been reported for vinyl and methacryl functional silanes (5,6). Generally, the transition observed for the aminosilane at 0.15% by weight is an isolated monomer-associated monomer transition. However, as soon as the silanetriol of the aminosilane associate, the silanol condensation results due to the self-catalyzed condensation by the amine group. Hence, the isolated monomer-associated monomer transition becomes the isolated

monomer-oligomer transition. Obviously, the presence of oligomer will perturb the organization and orientation of the silane layers. Since the multilayer formation of silanes on smooth glass surface depends on its topological factors (31), the perturbation by the oligomer will decrease the ability to stack the silane molecules.

When silane layers become relatively thick, the so-called sea-island structure, where aggregates of silanes are observed by electron microscopy, appears on the glass surface (4). It is rather unexpected since according to the Raman and infrared studies (3) silanes, especially aminosilanes, are almost completely hydrolyzed at the concentration levels employed. However, aggregates formed by the smaller oligomers shown in figure 11 may be partially responsible for the sea-island formation. Another possible reason is the deposition of silanes as the solution between fibers evaporates since the sea-island structure can be minimized by filtering the interfiber solution (4).

CONCLUSIONS

Partially cured polyaminopropylsilsesquioxane and γ -APS in water have been studied. We proposed a multiply hydrogen-bonded structure for the intramolecular amine-silanol interactions through the study of isotope exchange in the partially cured solid as part of the mixture of amine structure. Although there are a few energetically stable conformations where there are no perturbations, the conformations are highly constrained. In the case of slight perturbations by the surrounding OH and NH groups, the proposed multiply hydrogen-bonded structure becomes the most probable conformation. The O.....N distance was experimentally determined to be 2.70 - 2.67 \AA and theoretically 2.49 - 2.45 \AA .

There are large amounts of free amine in the partially cured polymer. The frequency increase of the band at 931 cm^{-1} to 935 cm^{-1} and the disappearance of the 967 cm^{-1} band upon deuteration confirmed the existence of SiOH groups.

We have found that γ -APS in water at very dilute concentration levels (below 1% by weight) contains large amounts of silanetriols. When the concentration becomes 0.25% by weight or less, the aminosilane is mostly monomeric. The monomer-oligomer transition lies probably around 0.15% by weight. This transition appeared to be an important factor in determining the amount of adsorbed silane on the surface of glass fibers. We propose that this phenomenon is a general trend in surface modification with silane coupling agents and important in determining the optimum treatment conditions.

Hydrolyzed γ -APS forms aggregates of oligomers with submicron diameters, which can be broken up into individual oligomers by addition of an alcohol. Neutralized aminosilane dissolves quickly into water but forms micelles of unhydrolyzed silanes. It hydrolyzed gradually over long periods of time. When excess acid was added to γ -APS, the rate of hydrolysis was much faster and behaved similarly to the neutral silanes with respect to the formation of silanetriols.

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FIGURE CAPTIONS

Figure 1. Deuteration of partially cured polyaminopropylsilsesquioxane. A; a 20% by weight aqueous solution of γ -aminopropyltriethoxysilane was deposited on an AgBr plate and dried at room temperature with relative humidity of $50 \pm 5\%$ for 1 hr. B; the partially cured polymer on the AgBr plate was exposed to D_2O vapor for 15 min. and then dried in nitrogen atmosphere for an additional 15 min.

Figure 2. Protonation of a partially cured deuterated polyaminopropylsilsesquioxane. A; a 20% by weight D_2O solution of γ -aminopropyltriethoxysilane was deposited on an AgBr plate and dried at room temperature in nitrogen atmosphere for 1 hr. B; the partially cured deuterated polymer on the AgBr plate was exposed to H_2O vapor for 15 min. and then dried in nitrogen atmosphere for an additional 15 min.

Figure 3. Effect of dry air on the structure of a partially cured polyaminopropylsilsesquioxane prepared from 20% by weight aqueous solution of γ -aminopropyltriethoxysilane deposited on an AgBr plate. A; an incompletely cured polymer which was dried at room temperature with relative humidity $50 \pm 5\%$ for 1 hr. B; the polymer kept in a closed glass vial at room temperature for 130 hrs. with dry air controlled by P_2O_5 . C; the difference spectrum (B-A).

Figure 4. Effect of humid air free of CO_2 on the structure of a partially cured polyaminopropylsilsesquioxane prepared from 20% by weight aqueous solution of γ -aminopropyltriethoxysilane deposited on an AgBr plate. A; a partially cured polymer which was dried at room temperature with relative humidity $50 \pm 5\%$ for 1 hr. B; the polymer kept in a closed glass vial at room temperature for 130 hrs. with humid air controlled by dilute KOH aqueous solution in order to eliminate the effect of CO_2 in air. C; the difference spectrum (B-A).

Figure 5. Same as the figure 4 except the AgBr plate was coated with polyethylene in order to eliminate the contact between the AgBr and the silane film. Also, only water was used to create air saturated with water.

Figure 6. Raman spectra of γ -APS in water at concentrations of A; 10% by weight and B; 0.5% by weight. The laser output power of 300mW and the spectral resolution of 5 cm^{-1} were used for both spectra.

Figure 7. Relative Raman intensity I_{712}/I_{881} vs the concentration of silane solutions obtained for γ -APS in water.

Figure 8. Amount of adsorbed ^{14}C -labeled γ -APS from aqueous solution at various concentration (from reference 4) and the relative Raman intensity I_{712}/I_{881} read from figure 7.

Figure 9. Raman spectra of γ -APS at 5% by weight aqueous solutions. A; γ -APS was simply dissolved into water. B; γ -APS was neutralized first with slightly excess acetic acid and then dissolved into water.

Figure 10. Relative Raman intensity I_{712}/I_{1048} vs the mole ratio as acetic acid/ γ -APS. The aqueous solutions were 5% by weight of γ -APS.

Figure 11. Mass adjusted Raman intensity of the stoichiometric acetic acid/ γ -APS mixture dissolved into water as a function of hydrolysis time (5%).

O: trialkoxysilane ●: ethanol Δ: silanetriol

Figure 12. Hydrodynamic radii of γ -APS in water vs concentration.

O: as received ●: vacuum distilled prior to use

Figure 13. Possible conformation with total conformational energy of -26.3 kcal/mole .

Figure 14. Possible conformation with total conformational energy of -26.6 kcal/mole .

Figure 15. Possible conformation with total conformational energy of -27.7 kcal/mole .

Figure 1

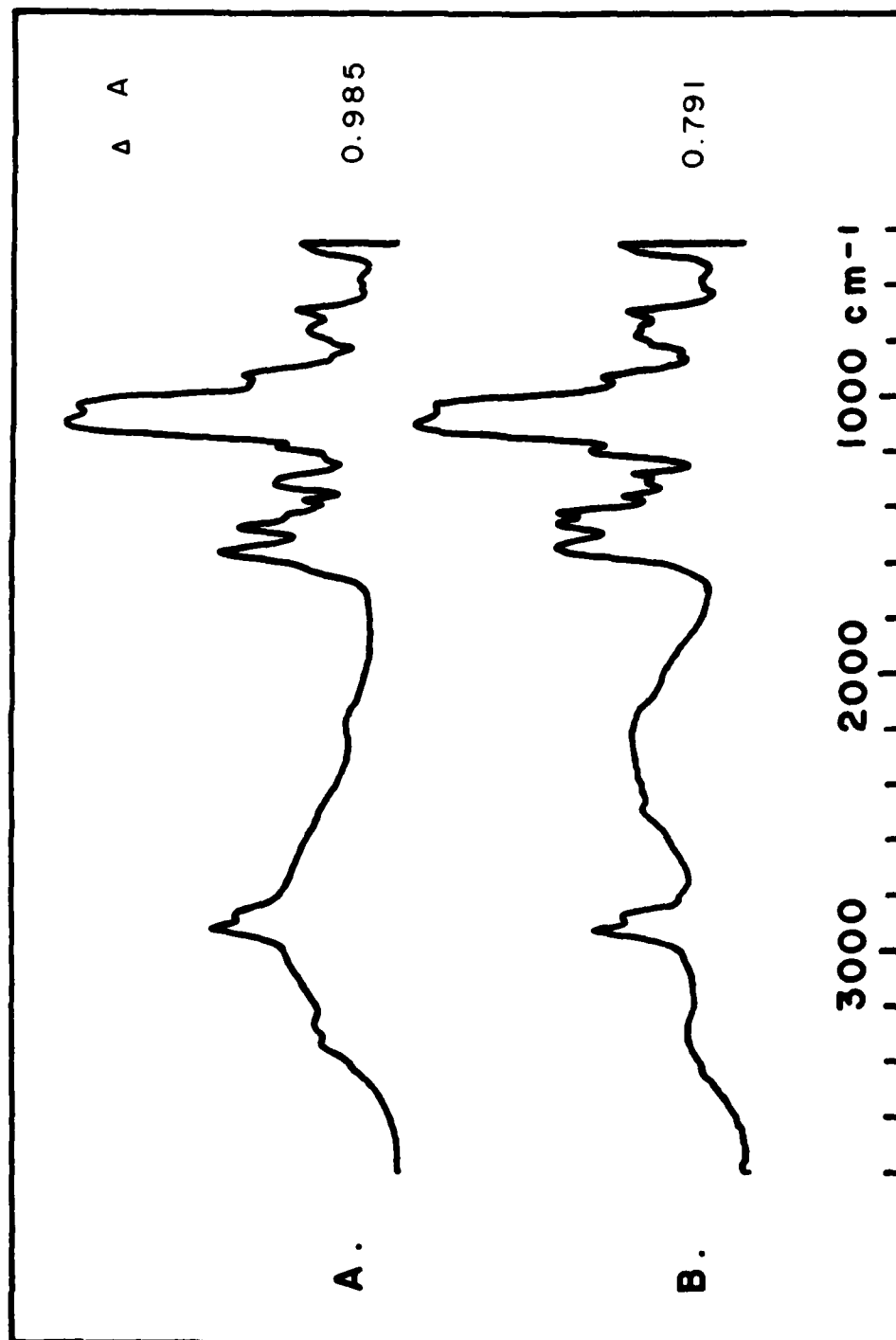


Figure 2

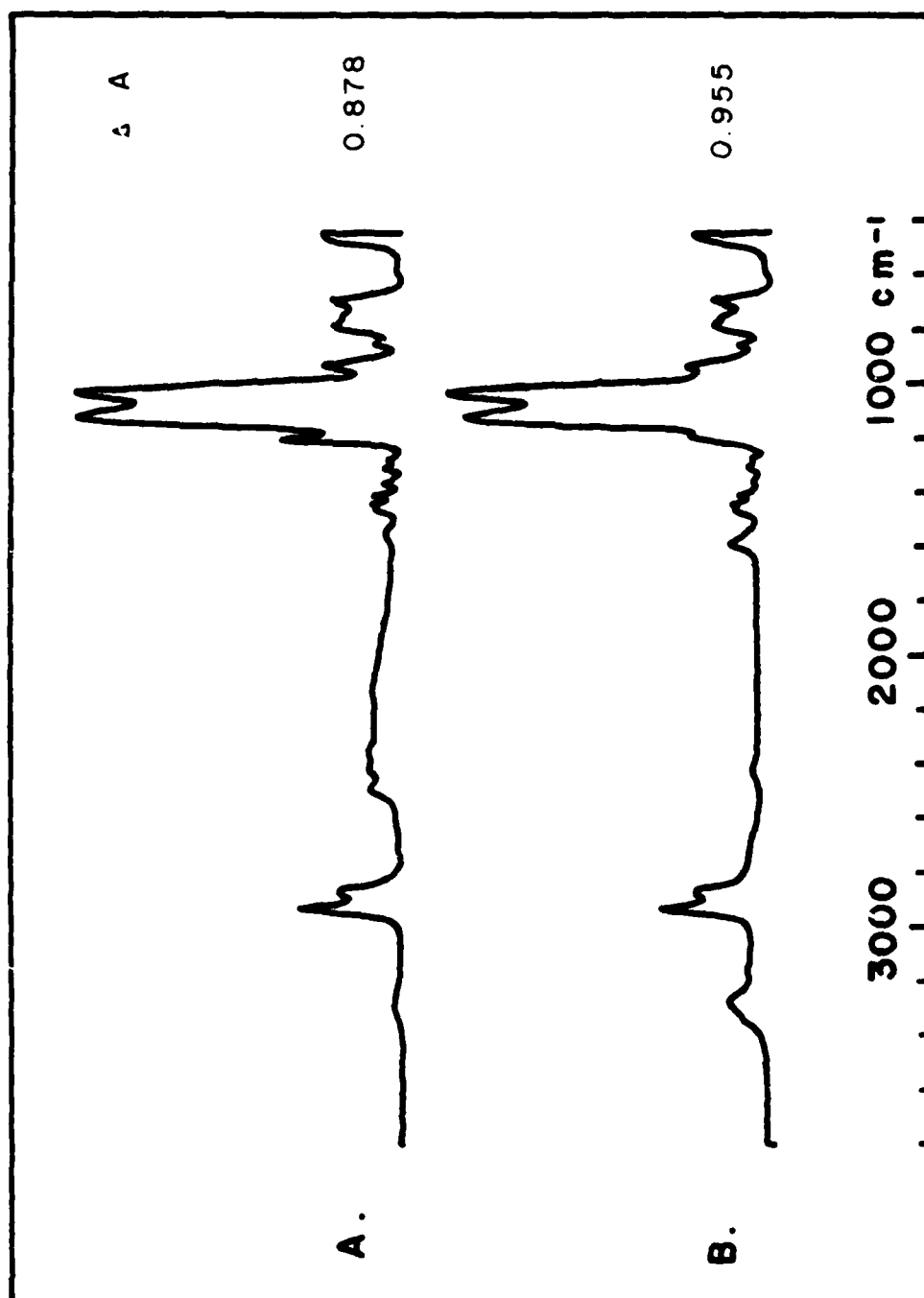


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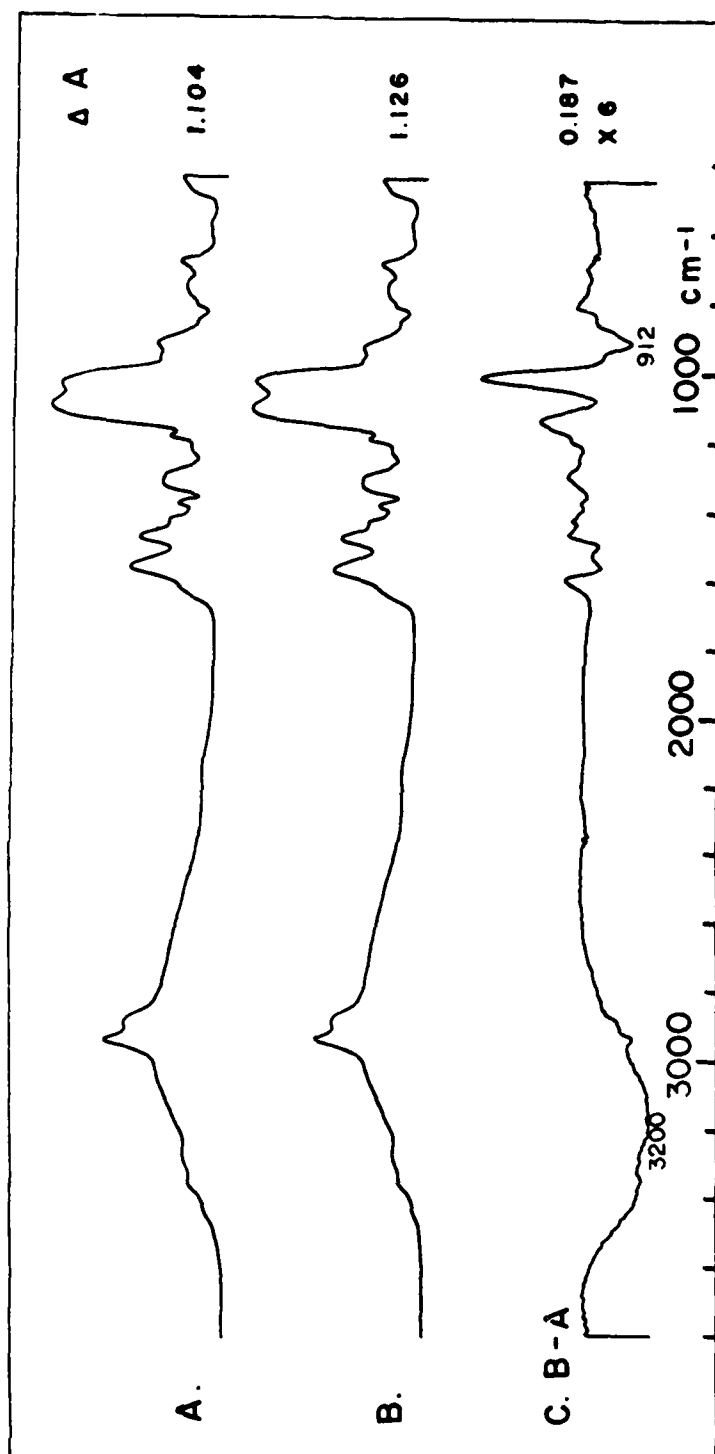


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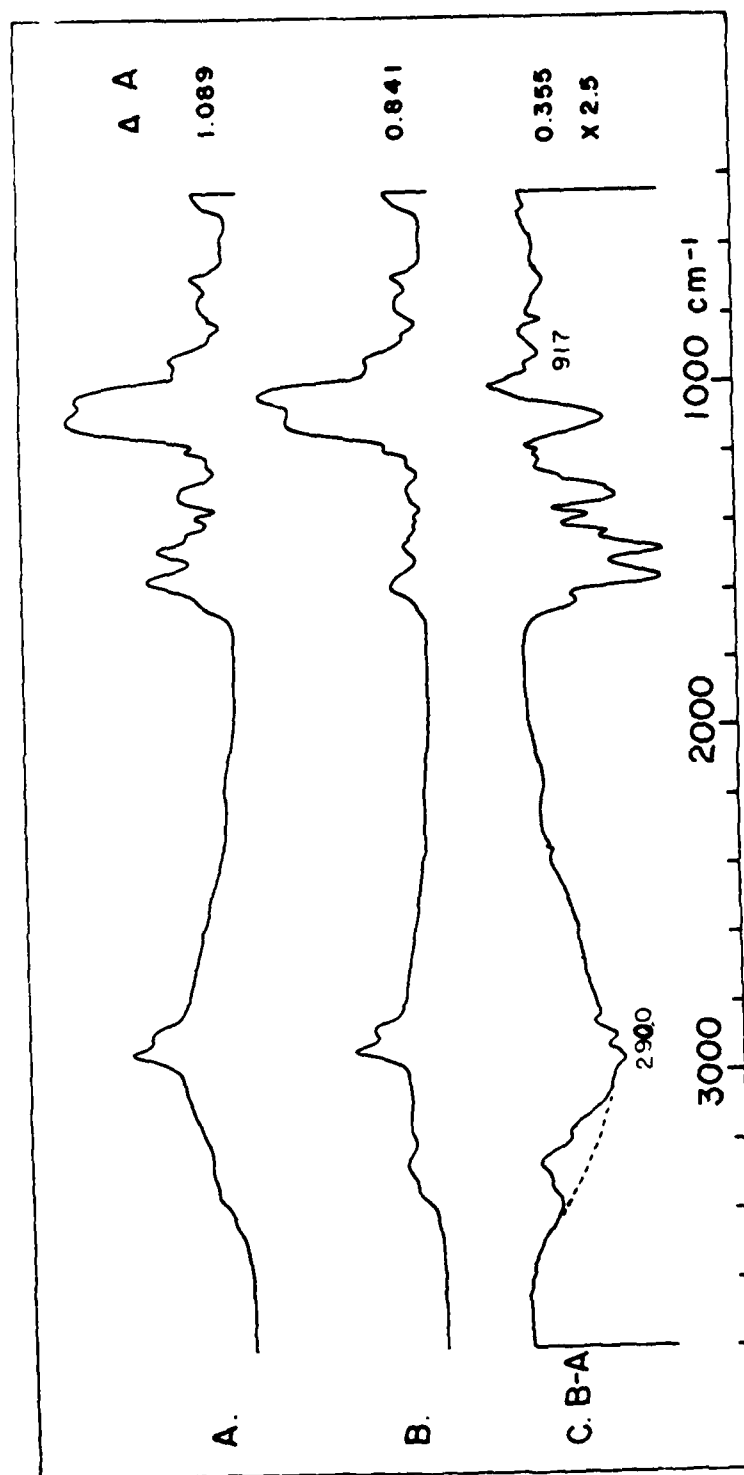


Figure 5

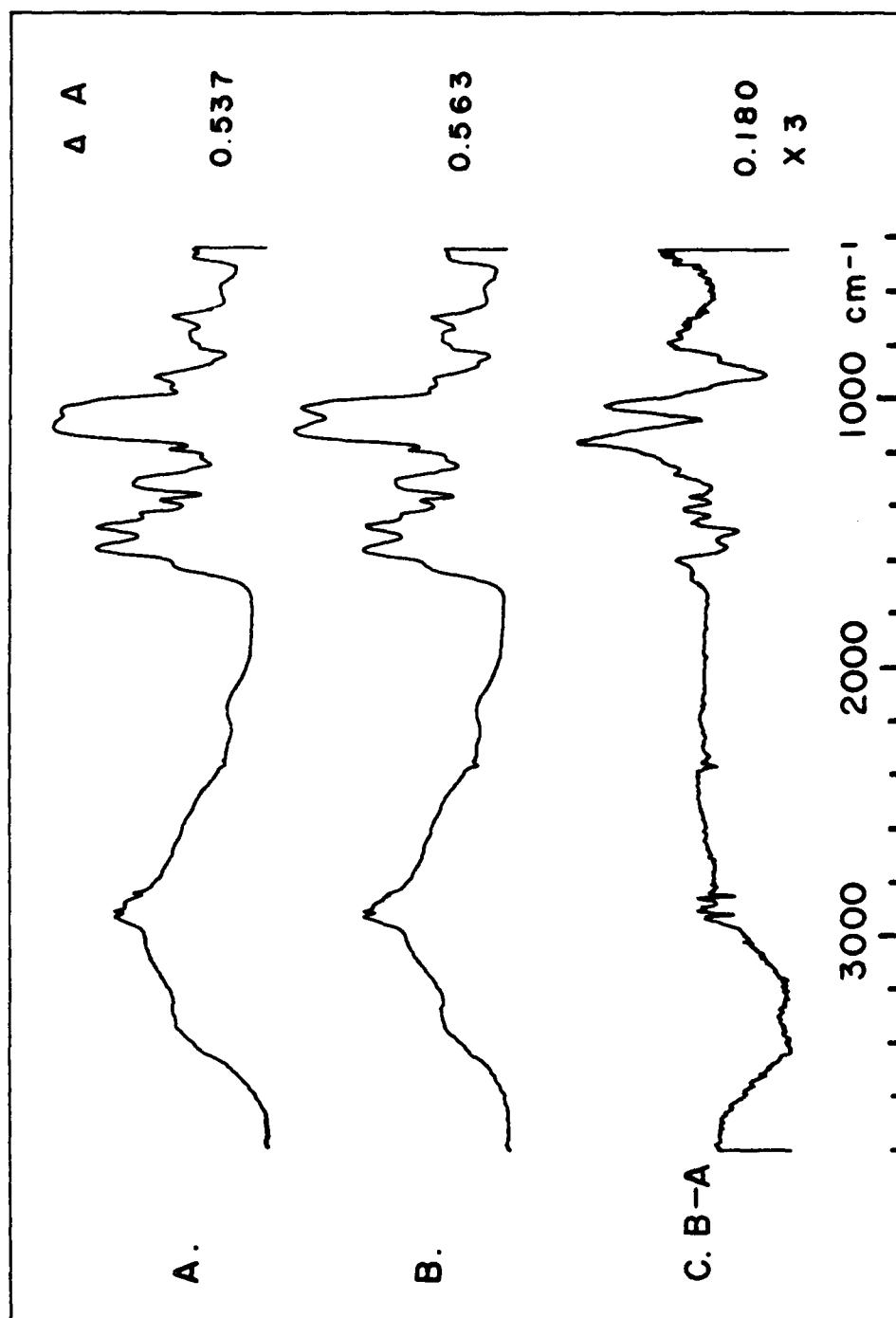


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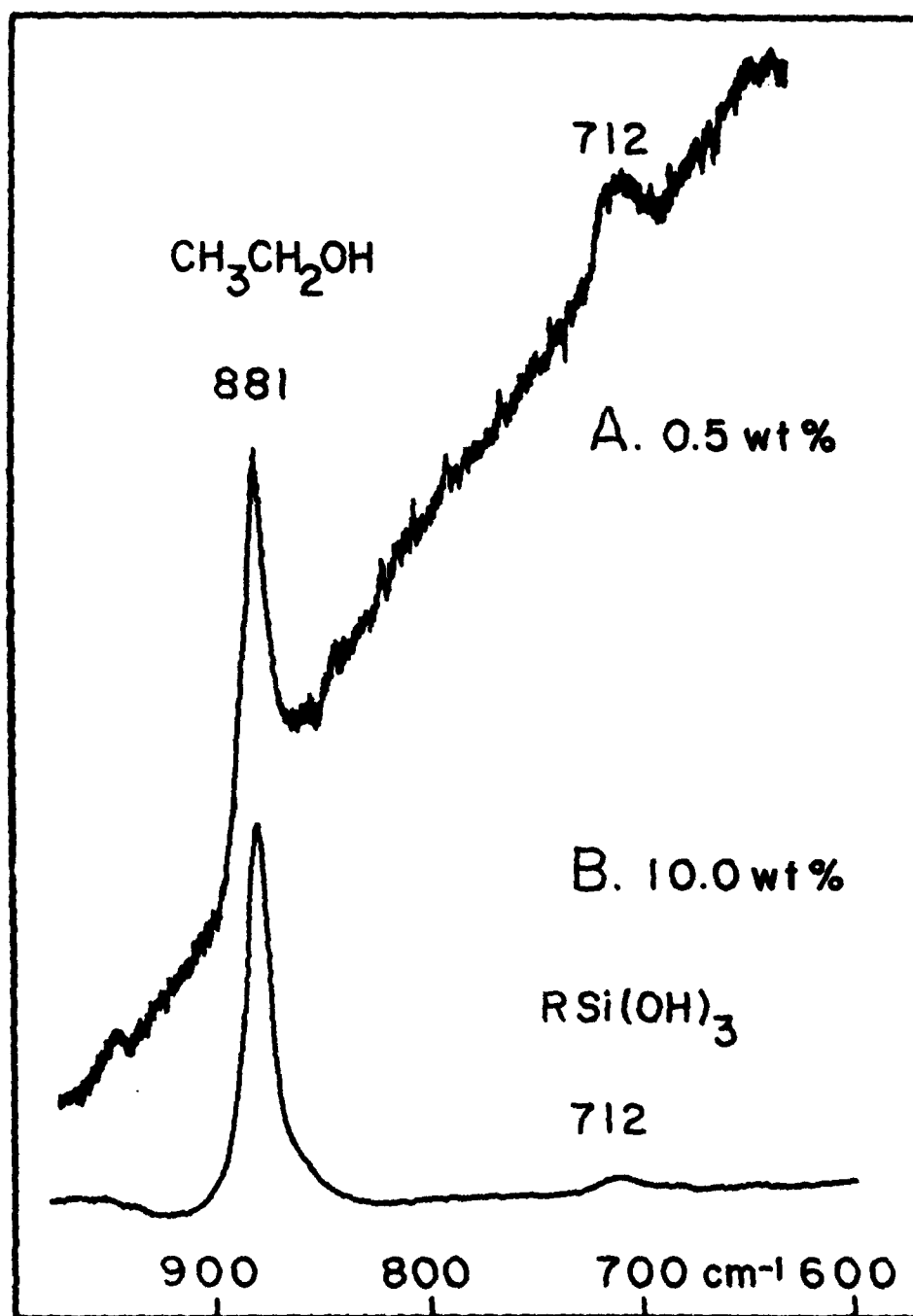


Figure 7

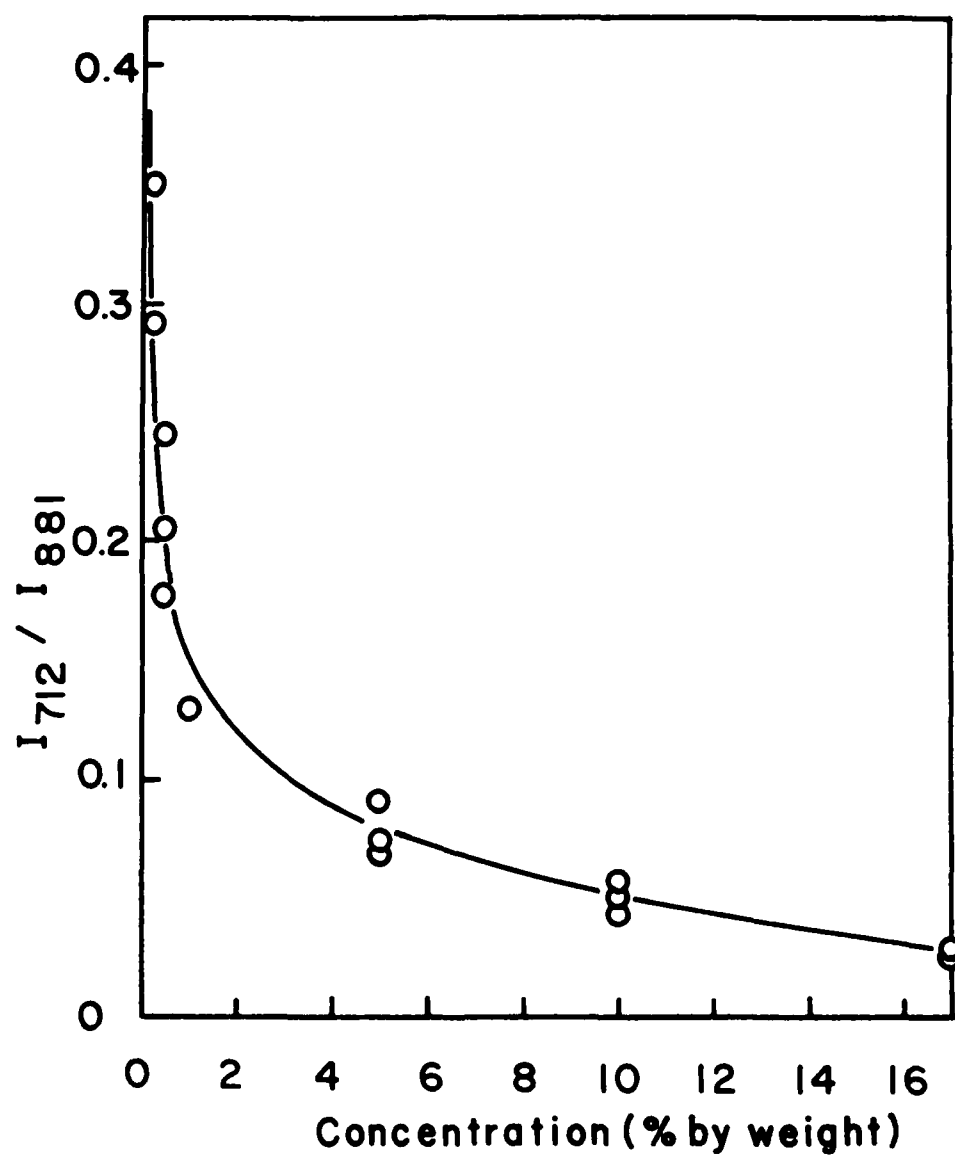


Figure 8

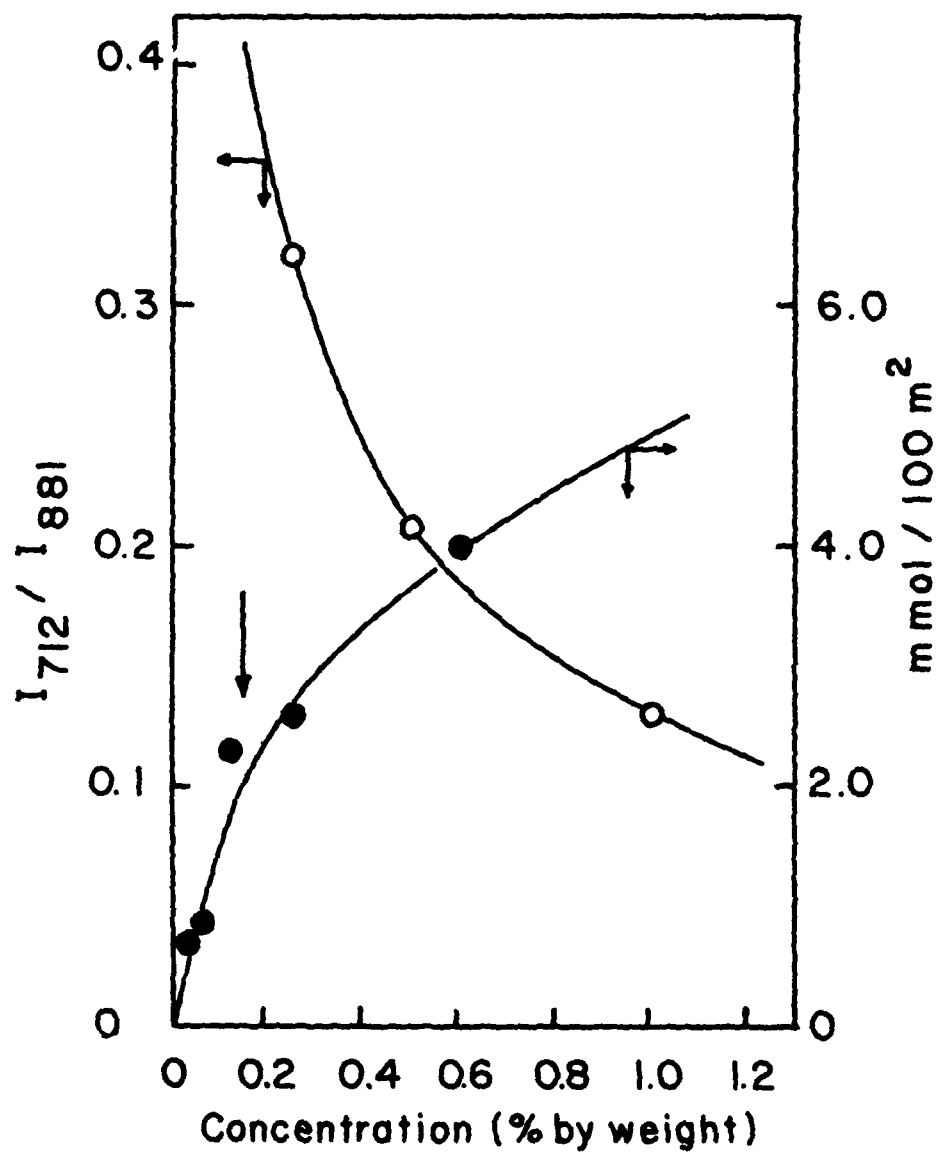


Figure 9

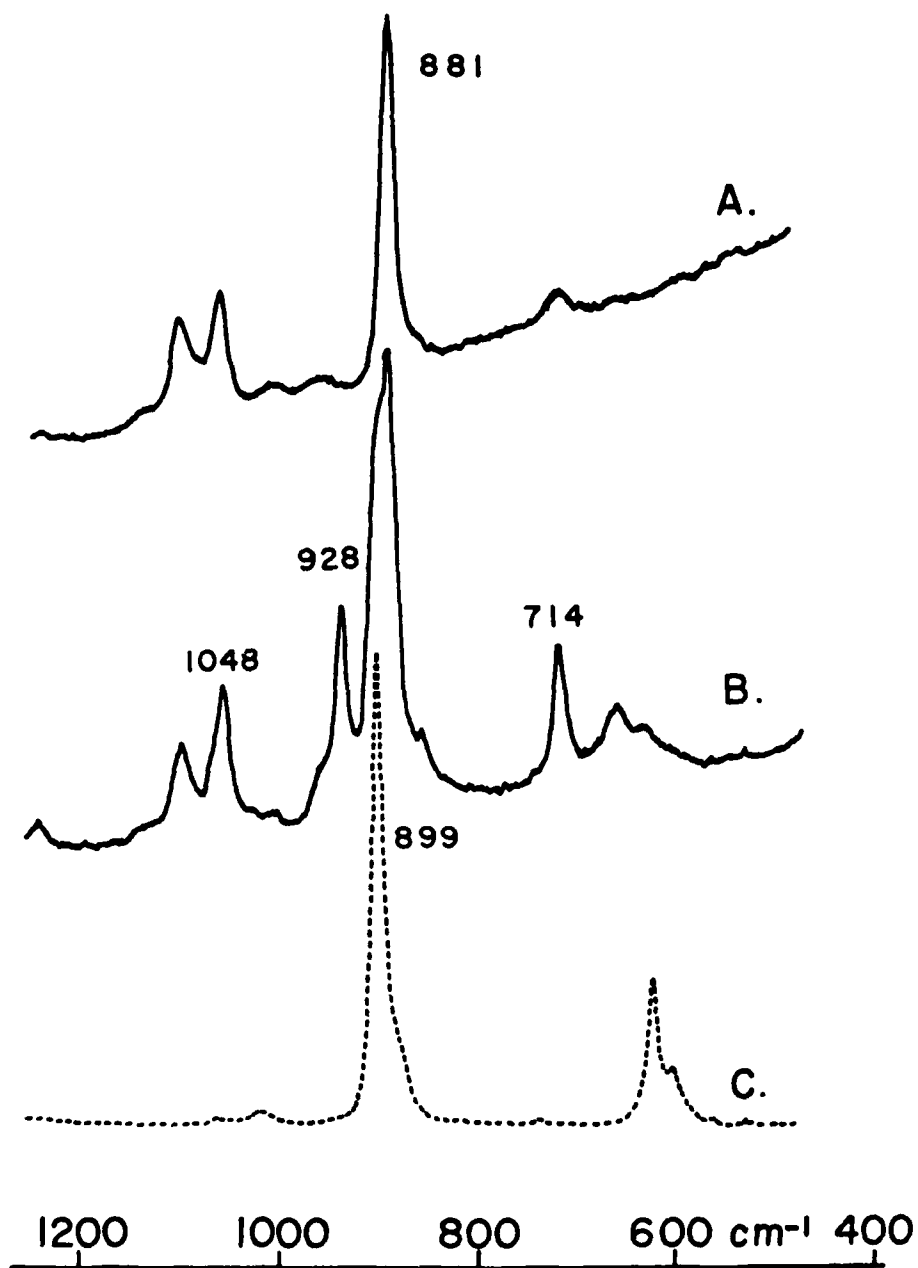


Figure 10

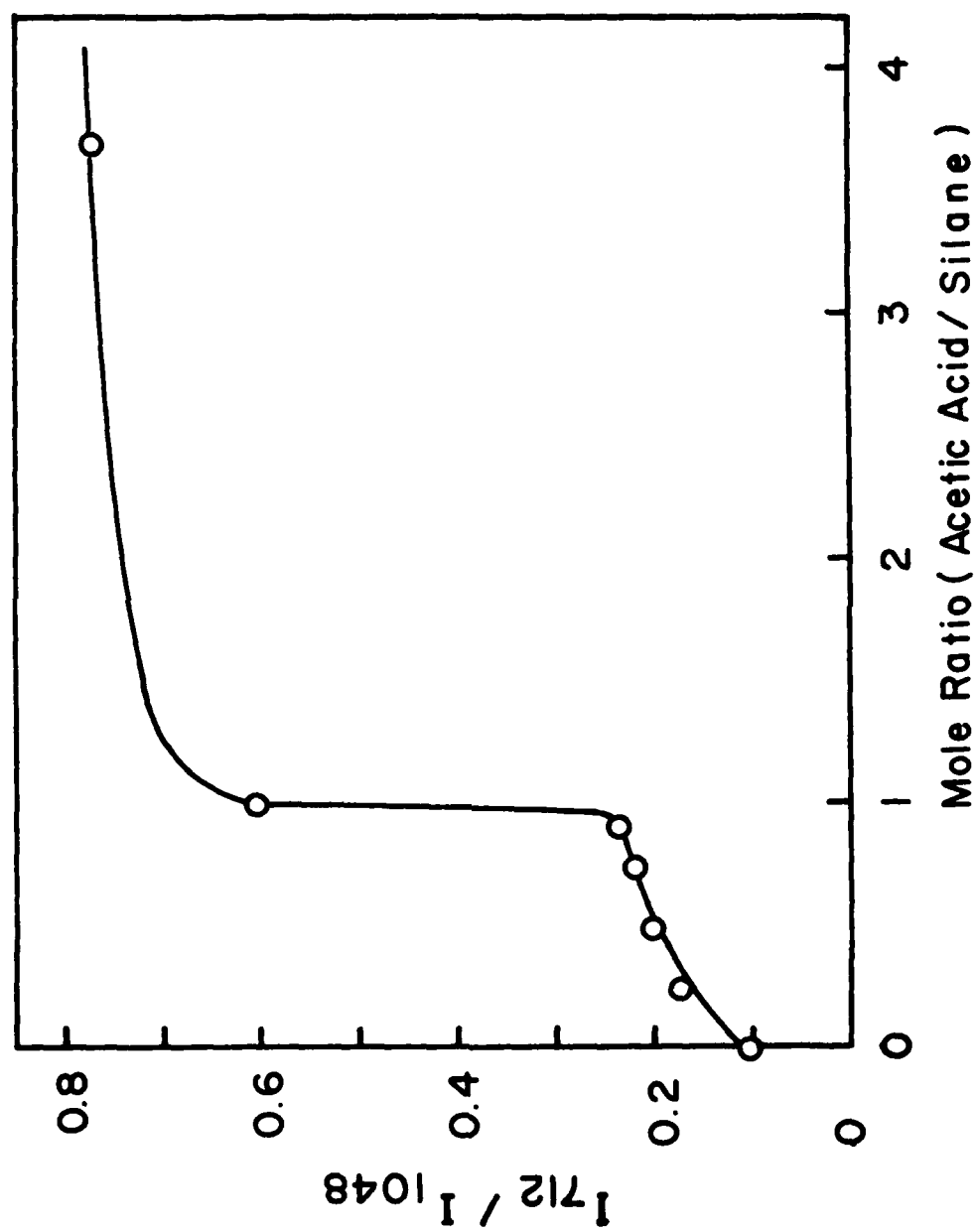


Figure 11

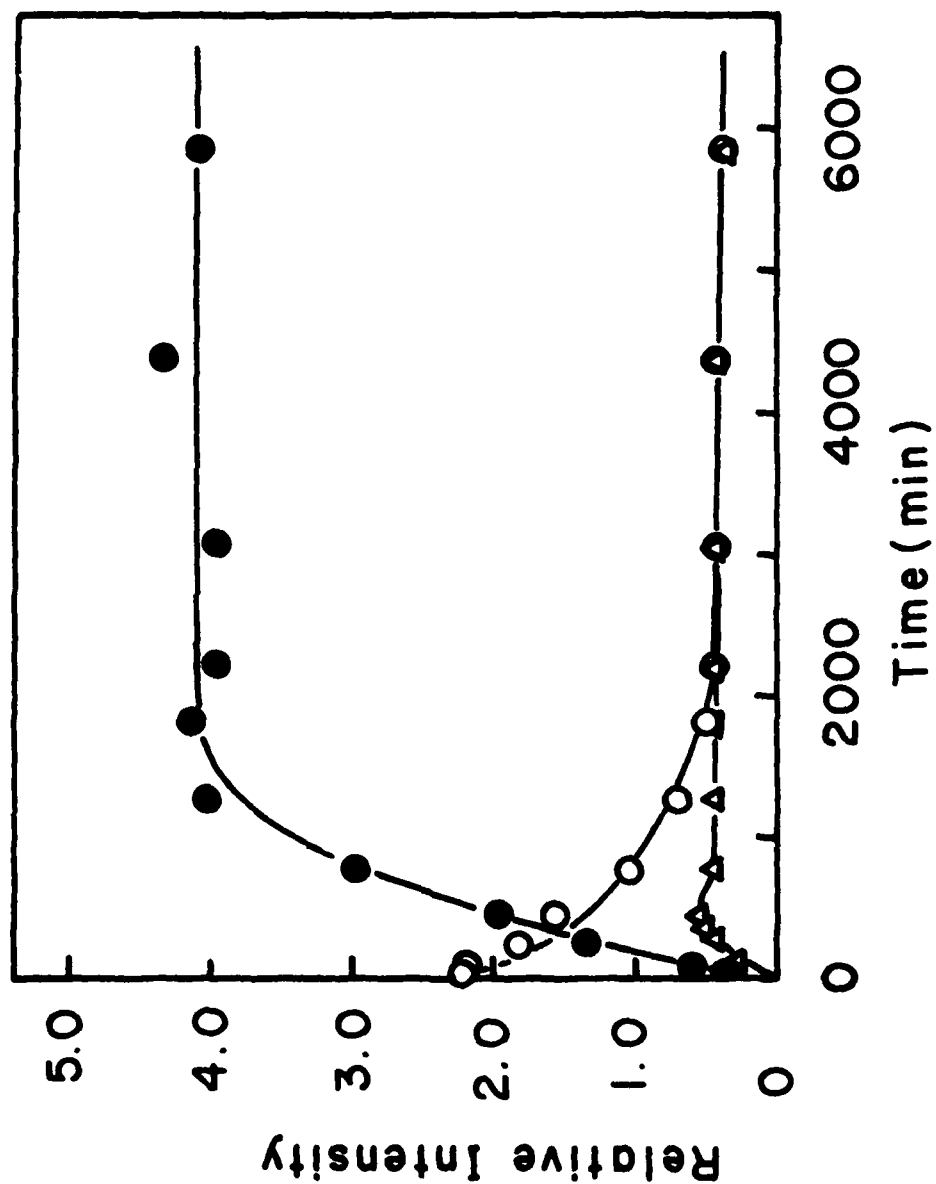


Figure 12

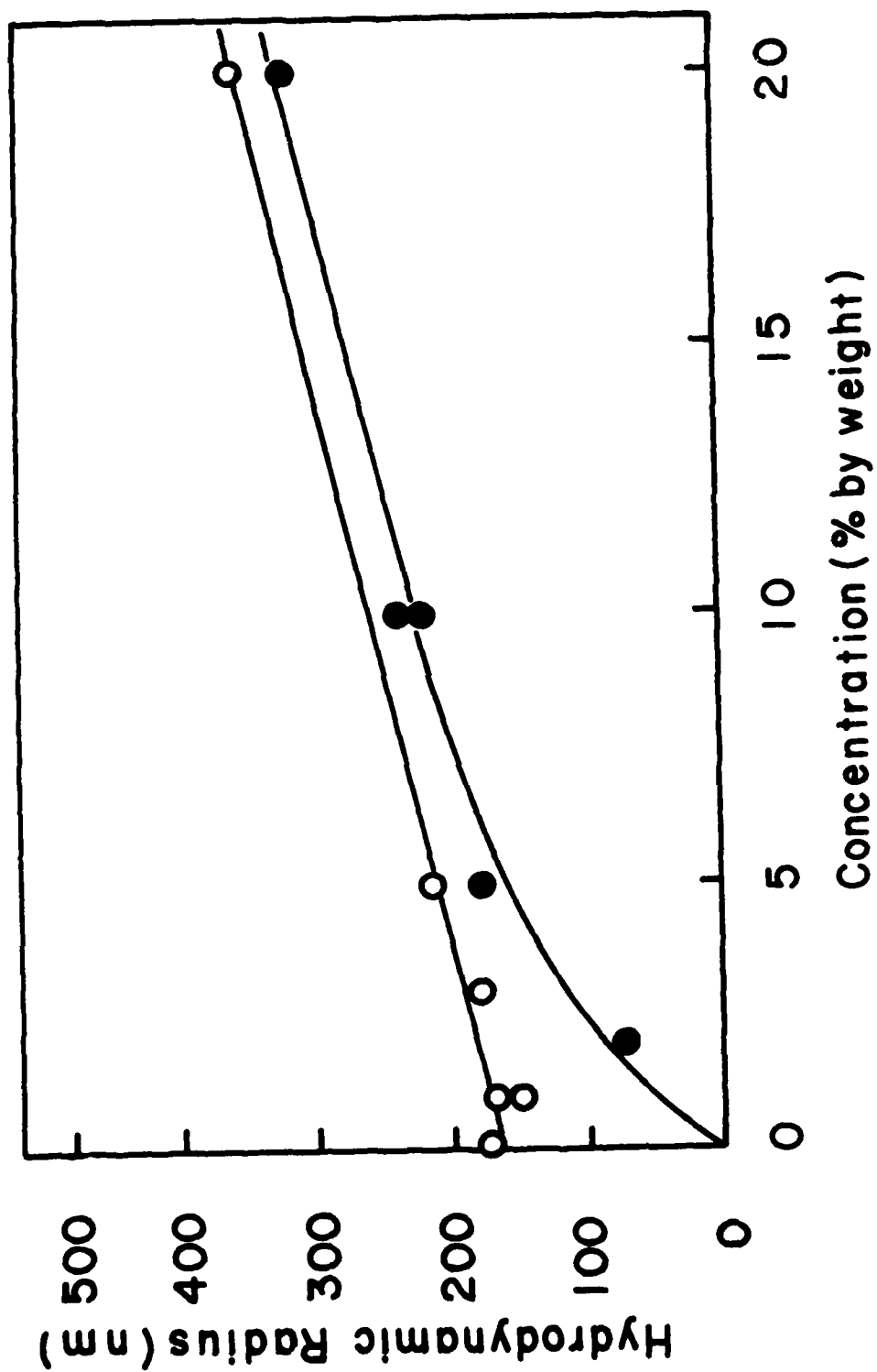


Figure 13

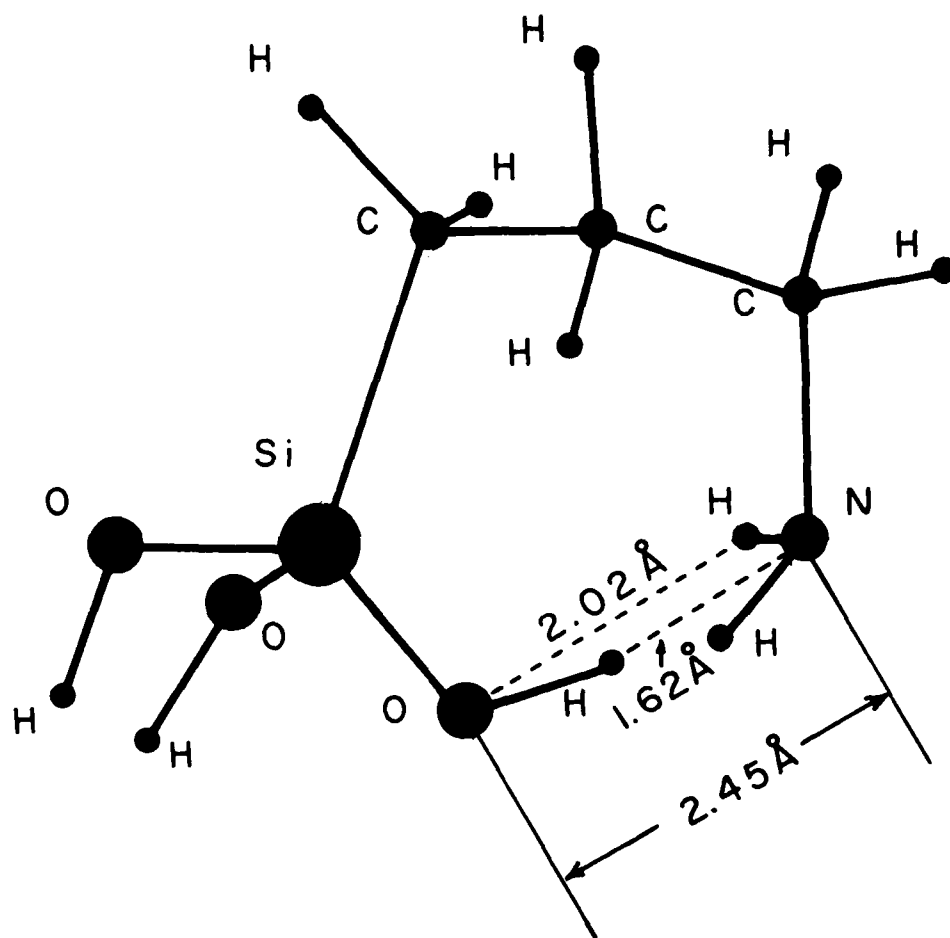


Figure 14

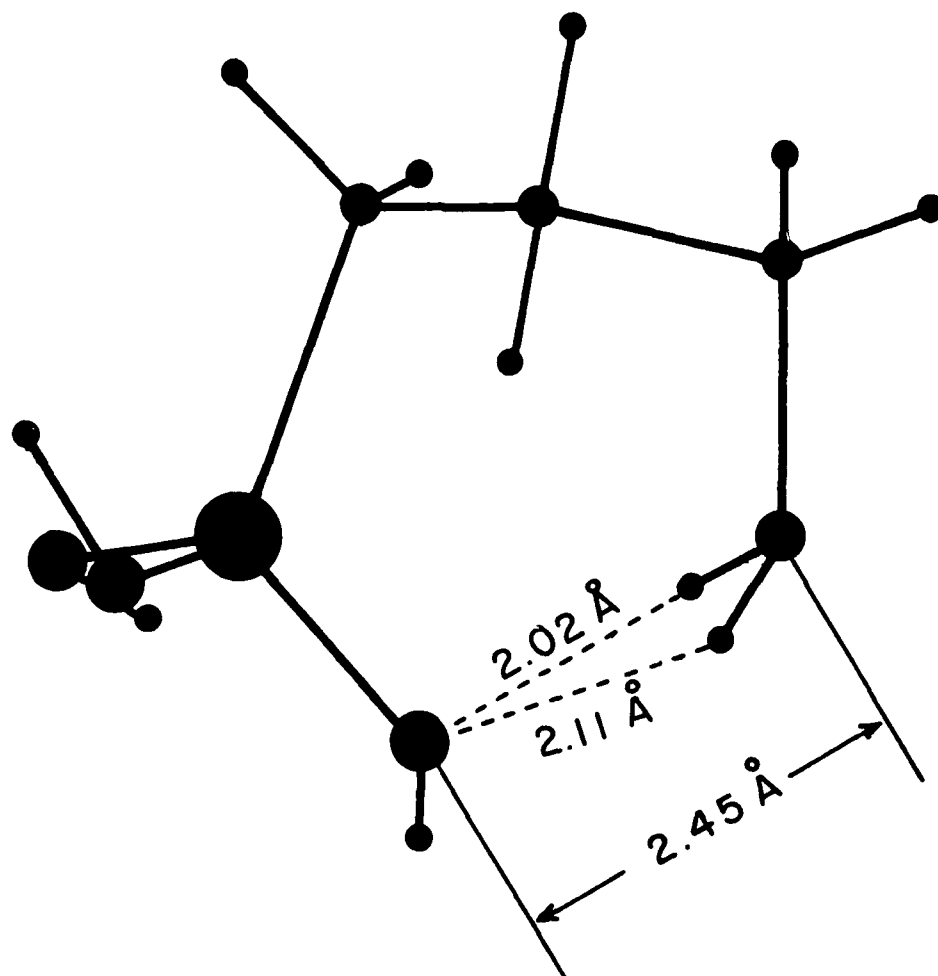
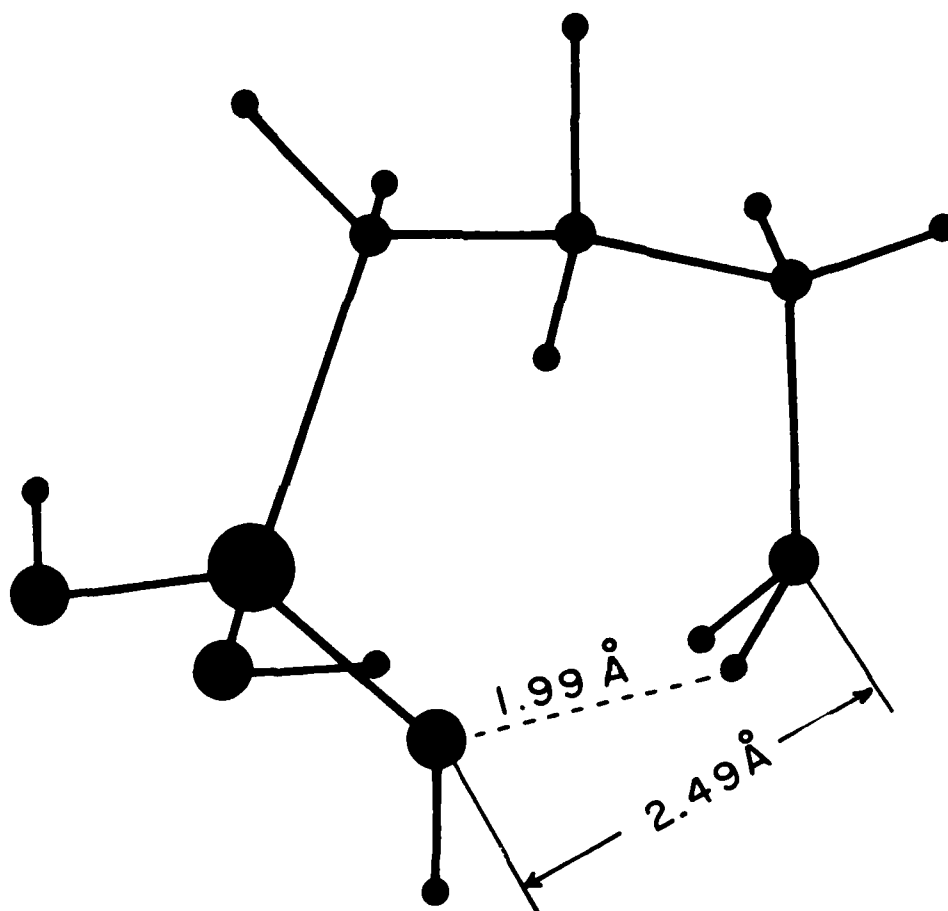


Figure 15



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